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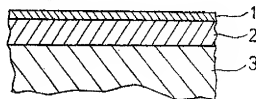
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(54) 【発明の名称】 磁気記録媒体

(57) 【要約】

【目的】 優れた耐磁性、スチル耐久性及び電磁変換特性を有した薄膜型磁気記録媒体を提供する。

【構成】 非磁性支持体3上にCoを主成分とする強磁性薄膜層2を形成し、この強磁性薄膜層2上に炭化水素を原料とするダイヤモンドライクカーボン層1を形成した磁気記録媒体において、前記強磁性薄膜層膜厚方向における表面側1/3内の磁束最大濃度が10at%以上30at%未満であり、前記ダイヤモンドライクカーボン層の膜厚が20Å以上100Å未満である磁気記録媒体。



## 【特許請求の範囲】

【請求項1】 非磁性支持体上にCoを主成分とする強磁性薄膜を形成し、この強磁性薄膜層上に炭化水素を原料とするダイヤモンドライクカーボン層を形成した磁気記録媒体において、前記強磁性薄膜層膜厚方向における表面側1/3内の炭素最大濃度が10at%以上30at%未満であり、前記ダイヤモンドライクカーボン層の膜厚が20Å以上100Å未満であることを特徴とする磁気記録媒体。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】本発明は、Co系強磁性薄膜層からなる磁気記録媒体、例えば磁気テープに関するものである。

## 【0002】

【従来の技術】従来より磁気記録媒体としては、非磁性支持体上に $\gamma\text{-Fe}_2\text{O}_3$ 、Coを含有する $\gamma\text{-Fe}_2\text{O}_3$ 、 $\text{CrO}_2$ 等の酸化物強磁性粉末あるいは、Fe、Co、Ni等を主成分とする合金磁性粉末等の粉末磁性材料を塩化ビニル系共重合体、ポリエステル樹脂、ポリウレタン樹脂等の有機バインダー中に分散せしめた磁性塗料を塗布・乾燥することにより作製される塗布型の磁気記録媒体が広く使用されている。

【0003】これに対して、真空蒸着、スパッタリング、イオンプレーティング等の方法によって形成される強磁性薄膜は、高密度記録用磁気記録媒体として検討されている。これらの強磁性薄膜は抗磁力、角形比に優れているばかりではなく、塗布型媒体では必須である有機バインダーを磁性層中に含有しないため残留磁束密度も高い。更に磁性層の厚さを極めて薄くすることができるため、再生時の厚み損失も少ない。

【0004】このように優れた電磁変換特性を有する反面、これらの強磁性薄膜は金属材料から形成されているため、塗布型媒体と比較して腐食され易く、またスチル耐久性も悪い。

【0005】これらの性能を改良するために、最近スパッタによるアモルファスカーボンやプラズマCVDによるダイヤモンドライクカーボンの保護層が研究されている。これらの強磁性薄膜は上記の性能を向上させる効果はあるものの、その膜厚に伴うスペーシング損失により、とくに短波長出力が影響を受け減少する。

【0006】近年MPテープは薄膜化、微粒子化、表面平滑化等の改良により短波長出力は向上し、MEテープのそれに近づいてきている。従ってMEテープの最大の弱点である短波長出力のスペーシング損失による低下は極力少なくしなければならないが、これまでの所100Å以上の硬質炭素膜の形成が必要であり、そのため短波長出力が2dB以上低下していた。

## 【0007】

【発明が解決しようとする課題】本発明の目的は、上記

のような問題点を解決し、優れた耐磁性、スチル耐久性および電磁変換特性を有する薄膜型磁気記録媒体を提供することにある。

## 【0008】

【課題を解決するための手段】上記目的は、非磁性支持体上にCoを主成分とする強磁性薄膜層を形成し、この強磁性薄膜層上に炭化水素を原料とするダイヤモンドライクカーボン層を形成した磁気記録媒体において、前記強磁性薄膜層膜厚方向における表面側1/3内の炭素最大濃度が10at%以上30at%未満であり、前記ダイヤモンドライクカーボン層の膜厚が20Å以上100Å未満であることを特徴とする磁気記録媒体によって達成される。

## 【0009】

【作用】本発明は、前記目的を達成するために鋭意研究の結果、得られたもので、通常蒸着時に酸素導入にともなう磁性層表面側1/3内の炭素最大濃度を、10at%以上30at%以下とすることによって、非磁性酸化物層に起因するスペーシング損失を減少させ、さらに磁性層表面にダイヤモンドライクカーボン層を20Åから100Å形成し、ダイヤモンドライクカーボン層に起因するスペーシング損失の増大を最小限に抑えつつ耐磁性、スチル耐久性を向上させることを特徴とする。

【0010】以下、本発明を詳細に説明する。

【0011】本発明の磁気記録媒体は、図1に示すように、非磁性支持体3上に強磁性薄膜2が蒸着により形成されており、更にその上にダイヤモンドライクカーボン層1が形成されている。以下に磁気記録媒体について詳述する。

## 【0012】(a) 非磁性支持体

本発明に用いられる前記非磁性支持体の素材としては、ポリエチレンテフタレート、ポリエチレン-2,6-ナフタレート等のポリエステル類、ポリプロピレン等のポリオレフィン類、セルローストリアセテート、セルロースダイセテート等のセルロース誘導体、ポリアミド、芳香族ポリアミド、ポリイミド、ポリフェニレンサルファイド、ポリエーテルエーテルケトン、ポリカーボネートなどのプラスチックが使用される。

【0013】前記非磁性支持体には、みみず状突起や粒状突起を形成することにより、強磁性金属薄膜層の粗さあるいは形状をコントロールすることができる。

【0014】前記みみず状突起は、例えば非磁性基板上に高分子物質を塗布して乾燥した後、延伸することにより形成することができる。前記粒状突起は、高分子フィルム製膜時に粒径50Å〜3000Å程度の無機微粒子を分散させて内部にこれを保持するか、またはバインダー中に有機微粒子またはシリカ、金属の微粒子を分散させ非磁性支持体の下引き層として塗布または付着させることにより形成することができる。この粒状突起の高さは、50Å〜1000Å、さらに好ましくは100Å〜500Åである。密度は $10^{-2}$ 〜 $10^0$ 個/ $\text{mm}^2$ であることが好ましい。これらの突

起を形成することにより耐久性、走行性が改善される。

【0015】前記非磁性支持体の形態は、テープ、シート、カード、ディスク等いずれでもよく、磁気記録媒体としての最終的な形態に応じてそれぞれの材料が選択される。

【0016】これらの非磁性支持体の厚みは、テープ、シート状の場合は約3〜100 $\mu\text{m}$ 程度、好ましくは4〜50 $\mu\text{m}$ であり、ディスク、カード状の場合は30 $\mu\text{m}$ 〜10mmの範囲のものをを用いることができる。

【0017】(b) 強磁性薄膜層

前記非磁性支持体上に強磁性薄膜層が設けられる。

【0018】本発明に用いられる磁性材料はCoもしくはCoを主成分とする合金系磁性材料であれば、従来から使用されている公知の磁性材料を使用することができる。本発明の方法に用いられる磁性材料の具体例としては、Fe-Co、Fe-Co-Ni、Co-Ni、Co-Cu、Co-Au、Co-Y、Co-La、Co-Pr、Co-Gd、Co-Sm、Co-Si、Co-Pt、Co-Cr、Fe-Co-Cr、Co-V、Co-W、Co-Mn、Co-Ti、Co-Ni-Cr、Fe-Co-Ni-Cr等を挙げることができる。

【0019】本発明の磁気記録媒体における強磁性薄膜層には、Coが全金属原子量の70重量％以上含有するのが好ましい。Coの含有量が前記範囲外にあると保磁力や残留磁束密度が低下し、電磁変換特性の悪化をもたらすことができる。

【0020】更に強磁性薄膜層中には酸素が含有される。

【0021】通常、蒸着時に酸化性ガスを低入射気流側に導入することにより、前記強磁性薄膜層の表面近傍に酸素濃度の高い酸化物層が形成される。酸化性ガスの導入量により、前記酸化物層の酸素最大濃度、酸化物層の膜厚が変化する。

【0022】酸化性ガスの導入量が少な過ぎると酸素最大濃度、酸化物層の膜厚が減少し、走行耐久性、耐酸性、スチル耐久性の悪化をもたらす、更に磁性層内部の酸素濃度も低いため保磁力、出力、S/Nも低くなる。

【0023】これに対し酸化性ガスの導入量が多過ぎると保磁力が高くなるものの表面酸化物層の膜厚が増加し、出力が減少する。以上より耐久性、耐酸性、電磁変換特性等の特性がバランスよく良好な所定の酸化性ガス導入量が決定される。

【0024】このとき、表面酸化物層の酸素最大濃度は30〜50at%となり、また酸化物層の膜厚は50〜300 $\text{\AA}$ 程度となる。

【0025】前記強磁性薄膜層上にダイヤモンドライカーボン層をプラズマCVD装置で形成する際、強磁性薄膜層表面近傍の酸素は、負バイアス電圧の印加により水素や炭素と反応し $\text{H}_2\text{O}$ 、 $\text{CO}_2$ となりガスとして抜けていく。この結果ダイヤモンドライカーボン製膜後の表面近傍の酸素濃度は、製膜前のそれと比べ減少し

ベージング損失が低下し、電磁変換特性は向上する。ただし負バイアス電圧が高過ぎると異常放電を起こし、膜の堆積がされにくくなる。負バイアス電圧は、 $-100\text{V}$ 〜 $-3\text{KV}$ の範囲内が好ましい。

【0026】本発明において、ダイヤモンドライカーボン製膜後の強磁性薄膜層の表面側1/3内の酸素最大濃度は、10〜30at%、好ましくは10〜25at%である。表面側1/3内の酸素最大濃度が10at%未満では、保磁力が低い。また電磁変換特性が不十分であり、30at%を超えると表面酸化物層によるベージング損失により出力の低下をもたらす。

【0027】前記強磁性薄膜層の膜厚は、5000 $\text{\AA}$ 以下、好ましくは800〜3500 $\text{\AA}$ の範囲内である。

【0028】なお、強磁性薄膜層は複数層から構成されても良く、その場合強磁性薄膜層最上層の表面側1/3内の酸素最大濃度が10〜30at%である。

【0029】強磁性薄膜層を形成するには、前記非磁性支持体上に前記強磁性材料を蒸着させる。

【0030】蒸着法としては、真空蒸着法、イオンプレーティング法等を用いることができる。加熱は電子ビーム加熱法、抵抗加熱法、レーザービーム加熱法、誘導加熱法等を用いることができる。

【0031】蒸着時に使用する酸化性ガスとしては、酸素、酸素の同素体及び酸素の活性種から選ばれる少なくとも1種を含むガスであればよい。また、これらのガスと併用できる他のガスとして、例えば窒素( $\text{N}_2$ )ガス、ヘリウムガス( $\text{He}$ )、キセノンガス( $\text{Xe}$ )、ラドンガス( $\text{Rn}$ )、アルゴン( $\text{Ar}$ )、ネオン( $\text{Ne}$ )等の不活性ガス、一酸化炭素( $\text{CO}$ )、炭酸ガス( $\text{CO}_2$ )、水素( $\text{H}_2$ )、水蒸気( $\text{H}_2\text{O}$ )を単独で、若しくは2種以上を混合して併用できる。

【0032】(c) ダイヤモンドライカーボン層  
前記強磁性薄膜層上にダイヤモンドライカーボン層が設けられる。

【0033】本発明におけるダイヤモンドライカーボン層はプラズマCVD装置を使用して、メタン、エタン、プロパン、ブタン、ペンゼン等の炭化水素ガスの分解により作製することができる。

【0034】前記ダイヤモンドライカーボン層は、電子構造は $\text{SP}^2$ 及び $\text{SP}^3$ であり、ダイヤモンド結合を含むアモルファス状態からなる膜であって、これはラマン分析、TEM制限視野回折及びESCAによる結合エネルギーの測定から判断することができる。

【0035】さらにビッカース硬度は、 $\text{Hv}=2000\sim3000\text{ (kg/mm}^2\text{)}$ と高く(NEC製MHA-400で測定)耐摩耗性に優れている。

【0036】前記ダイヤモンドライカーボン層の膜厚は、20〜100 $\text{\AA}$ 、好ましくは20〜50 $\text{\AA}$ の範囲内である。20 $\text{\AA}$ 未満では、耐酸性、スチル耐久性に効果が少なく、逆に100 $\text{\AA}$ を超えるとベージング損失が増大し出力の

低下をもたす。

【0037】(d)その他の層

本発明における磁気記録媒体は、磁気記録媒体の滑り性の改善、帯電防止、転写防止、耐熱性向上、耐摩耗性向上の目的で、前記非磁性支持体上に前記磁性薄膜層形成後及び／又は形成前に例えば公知の塗布方法、蒸着方法により、オーバーコート層やバックコート層を設けても良い。これらの塗布方法、蒸着方法は、例えば特開昭54-123922号、特開昭54-123923号、特開昭56-71284号、特開昭56-71286号、特開昭56-71287号、特開昭56-11626号、特開昭57-135442号の公開特許公報明細書に掲載されている。

【0038】バックコート層は塩化ビニル、塩化ビニル-酢酸ビニル、フェノール樹脂、ポリウレタン樹脂等のバインダー樹脂1種以上に、導電性カーボンブラックを1種、或は粒径又は化学的性質の違う種類のカーボンブラックを2種以上一緒に分散させるか別々に分散させた塗液を、非磁性支持体の強磁性薄膜が設けられる反対の面に塗布して形成する。分散時に使用される有機溶媒としては、シクロヘキサノン、トルエン、メチルエチルケトン、ベンゼン等がよく使用される。また、表面性または耐久性改善のために無機顔料をカーボンブラックと共に分散させてもよい。

【0039】オーバーコート層は潤滑剤として、パーフルオロポリエーテル、片末端活性パーフルオロポリエーテル、両末端活性パーフルオロポリエーテル、脂肪族またはその金属塩、脂肪族アミド、脂肪酸エステル、酸リン酸エステル、酸性リン酸アミン塩、ハイドロジェンホスファイト、パーフルオロアルキルカルボン酸またはその金属塩、パーフルオロアルキルカルボン酸エステル、パーフルオロアルキルカルボン酸、またはそのアンモニウム塩等が使用できる他、防錆剤（例えばアルキルフェノール、ハイドロキノノン、クレゾール、ナフトール類、トリアゾール類）や極圧剤（例えば、トリオレイルホスファイトのようなリン酸系極圧剤、硫黄ジメチルのようなチオウ系極圧剤、チオホスファイト類のような複合型極圧剤）を併用してもよい。

【0040】

【実施例】以下、本発明の実施例を示して本発明をさらに詳細に説明する。なお、本発明は以下の実施例に限定されることはなく、本発明の要旨の範囲内で適宜に変更できることは言うまでもない。

【0041】（実施例1）巻取り式真空蒸着機を用い、厚さ10.0μmのポリエチレンテレフタレートフィルム上にCo-Ni=80-20合金からなる磁性層θmax90度、θmin40度、膜厚2000Åの条件で形成した。なお最低入射角側から酸素を400SCCM導入しながら製膜した。

【0042】このサンプル上にプラズマCVD装置を用いダイヤモンドライカーカーボン層を形成した。製膜条件は、原料ガスにベンゼン・アルゴン1:1（モル比）混

合ガスを用い、10Paのガス圧条件で、プラズマ発生のRF出力を0.5KW、負バイアス電圧-2KVとして製膜を行い、ダイヤモンドライカーカーボン層厚が20Åとなるようにした。オージェデプスプロファイルによる磁性層表面側1/3内の酸素最大濃度は、20.2at%であった。

【0043】作製した磁気記録媒体のステル耐久性、耐酸性、電磁変換特性について測定した。

【0044】ステル耐久性；作製したサンプルを8mm幅に切断した後、8mmVTR用のカセットに入れ、市販のHi8VTRデッキを用い、はじめにカラーバー信号を録画しその後ステル再生を行って再生出力が初回値より-2dB低下するまでの時間で評価した。

【0045】耐酸性；テープ片を60°C、30%相対湿度中に1週間保存した後で、飽和磁化の減少率を測定した。

【0046】電磁変換特性；市販のHi8VTRデッキを用い、7MHzの出力を測定した。ただし、ここで比較例1のダイヤモンドライカーカーボン層を製膜しなかったサンプルの出力を0dBとした。

【0047】得られた結果を表1に示す。

【0048】（実施例2）実施例1において、ダイヤモンドライカーカーボン層の膜厚を30Åとした以外は、実施例1と同様にして磁気記録媒体を作製した。なおオージェデプスプロファイルによる磁性層表面側1/3内の酸素最大濃度は、20.8at%であった。

【0049】（実施例3）実施例1において、ダイヤモンドライカーカーボン層の膜厚を50Åとした以外は、実施例1と同様にして磁気記録媒体を作製した。なおオージェデプスプロファイルによる磁性層表面側1/3内の酸素最大濃度は、19.4at%であった。

【0050】（実施例4）実施例1において、ダイヤモンドライカーカーボン層の膜厚を100Åとした以外は、実施例1と同様にして磁気記録媒体を作製した。なおオージェデプスプロファイルによる磁性層表面側1/3内の酸素最大濃度は、19.6at%であった。

【0051】（実施例5）実施例1において、最低入射角側から酸素を200SCCM導入し、ダイヤモンドライカーカーボン層の膜厚を100Åとした以外は、実施例1と同様にして磁気記録媒体を作製した。なおオージェデプスプロファイルによる磁性層表面側1/3内の酸素最大濃度は、13.2at%であった。

【0052】（実施例6）実施例1において、最低入射角側から酸素を600SCCM導入し、ダイヤモンドライカーカーボン層の膜厚を20Åとした以外は、実施例1と同様にして磁気記録媒体を作製した。なおオージェデプスプロファイルによる磁性層表面側1/3内の酸素最大濃度は、27.3at%であった。

【0053】（比較例1）実施例1においてダイヤモンドライカーカーボン層を製膜しなかったこと以外は、実施例1と同様の条件で磁気記録媒体を形成した。なおオー

ジェデスプロファイルによる磁性層表面側1/3内の酸素最大濃度は、40.2at%であった。

【0054】（比較例2）実施例1において、ダイヤモンドライクカーボン層の膜厚を10Åとした以外は、実施例1と同様にして磁気記録媒体を作製した。なおオージェデスプロファイルによる磁性層表面側1/3内の酸素最大濃度は、31.9at%であった。

\*

\*【0055】（実施例3）実施例1において、ダイヤモンドライクカーボン層の膜厚を200Åとした以外は、実施例1と同様にして磁気記録媒体を作製した。なおオージェデスプロファイルによる磁性層表面側1/3内の酸素最大濃度は、17.1at%であった。

【0056】

【表1】

	酸素導入量 (SCCM)	DLC厚 (Å)	酸素最大濃度 (at%)	スチル耐久性 (min)	Φs減少率 (%)	7MHz出力* (dB)
実施例1	400	20	20.2	82	-11.6	+1.4
実施例2	400	30	20.8	120 <	-8.4	+1.3
実施例3	400	50	19.4	120 <	-6.9	+0.1
実施例4	400	100	19.6	120 <	-6.7	-1.1
実施例5	200	100	13.2	120 <	-7.3	-1.4
実施例6	600	20	27.3	96	-10.1	+0.3
比較例1	400	0	40.2	60 >	-15.3	0
比較例2	400	10	31.9	60 >	-14.2	+0.6
比較例3	400	200	17.1	120 <	-6.0	-2.6

\* ; ただし、比較例1（DLCを製膜しなかった）サンプルの出力を0dBとした。

【0057】（評価）以上の結果から明らかなように、強磁性薄膜膜厚方向における表面側1/3内の酸素最大濃度が10at%以上30at%未満であり、ダイヤモンドライクカーボン層の膜厚が20Å以上100Å未満である実施例1～6は出力が高く、またサーモ保存後の飽和磁化量Φs減少率も低い。更にスチル耐久性も良好である。

【0058】

【発明の効果】強磁性薄膜層上にダイヤモンドライクカーボン層を製膜する際、適当な負バイアス電圧を印加す

ることによって、製膜初期に強磁性薄膜層表面の酸素が水素、炭素と反応しガスとして抜けるためスベージング損失が低下する。更に20～100Åのダイヤモンドライクカーボン層によりスチル耐久性、耐熱性も向上する。

【図面の簡単な説明】

【図1】本発明の磁気記録媒体の要部拡大断面図である。

【符号の説明】

1 ダイヤモンドライクカーボン層

(6)

特開平7-6353

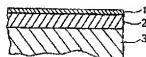
9

2 磁性層

10

\* \* 3 非磁性支持体 (基板)

【図1】



## CITED REFERENCE 1

## PATENT ABSTRACTS OF JAPAN

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G11B 5/72

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(21)Application number : 05-143775

(71)Applicant : KONICA CORP

(22)Date of filing : 15.06.1993

(72)Inventor : MIHO HIROAKI  
ITO KOICHI

## (54) MAGNETIC RECORDING MEDIUM

## (57)Abstract:

PURPOSE: To provide a thin film type magnetic recording medium having excellent corrosion resistance, still durability and electromagnetic transducing characteristics.

CONSTITUTION: A Co-based ferromagnetic thin film 2 is formed on a non-magnetic substrate 3 and a diamondlike carbon layer 1 is formed on the thin film 2 with hydrocarbon as starting material. The max. concn. of oxygen in the surface part of the ferromagnetic thin film corresponding to 5/3 of the thickness is 10 to <30 atomic% and the thickness of the diamondlike carbon layer is 20 to <100Å.



JAPANESE [JP:07-006353,A]

1. JP:07-006353,A(1995)

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT  
OF THE INVENTION TECHNICAL PROBLEM MEANS OPERATION  
EXAMPLE DESCRIPTION OF DRAWINGS DRAWINGS

[Translation done.]

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1.This document has been translated by computer. So the translation may not  
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CLAIMS

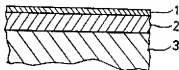
[Claim(s)]

[Claim 1] In a magnetic recording medium which formed a ferromagnetic thin  
film layer which uses Co as the main ingredients on a nonmagnetic substrate,  
and formed a diamond like carbon layer which uses hydrocarbon as a raw  
material on this ferromagnetic thin film layer, A magnetic recording medium,  
wherein oxygen maximum density in surface side 1 / 3 in said ferromagnetic  
thin film layer thickness direction is less than [ more than 10at%30at% ] and  
thickness of said diamond like carbon layer is not less than 20Å less than 100Å.

[Translation done.]

Drawing selection

Representative drawing



[Translation done.]



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DETAILED DESCRIPTION [Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the magnetic recording medium which consists of a Co system ferromagnetism thin film layer, for example, magnetic tape.

[0002]

[Description of the Prior Art] oxide ferromagnetic powder, such as gamma-Fe<sub>2</sub>O<sub>3</sub> which contains gamma-Fe<sub>2</sub>O<sub>3</sub> and Co on a nonmagnetic substrate as a magnetic recording medium conventionally, and CrO<sub>2</sub>, -- or, The magnetic recording medium of the coating mold produced by applying and drying the magnetic paint which made powder magnetic materials, such as alloy magnetic powder which uses Fe, Co, nickel, etc. as the main ingredients, distribute in organic binders, such as a VCM/PVC system copolymer, polyester resin, and polyurethane resin, is used widely.

[0003] On the other hand, the ferromagnetic thin film formed by methods, such as vacuum deposition, sputtering, and ion plating, is examined as a magnetic recording medium for high density recording. Since these ferromagnetic thin films are not only excellent in coercive force and a remanence ratio, but do not contain an indispensable organic binder in a magnetic layer by a coating mold medium, their residual magnetic flux density is also high. Since thickness of a magnetic layer can be made very thin, there is also little thickness loss at the time of reproduction.

[0004] Thus, while it has the outstanding magnetic parametric performance, since these ferromagnetic thin films are formed from the metallic material, as compared with a coating mold medium, it is easy to be corroded, and still durability is also bad [ ferromagnetic thin films ].

[0005] In order to improve such performances, the protective layer of the amorphous carbon by weld slag or the diamond like carbon by plasma CVD is studied these days. Although it is effective in raising the performance of the above [ these hard carbon films ], by the spacing loss accompanying the thickness, especially a short wavelength output receives influence and decreases.

[0006] The short wavelength output of MP tape improves by improvement of thin-film-izing, atomization, smooth-surface-izing, etc., and it has

been approaching it of a ME tape in recent years. Therefore, although the fall by the spacing loss of the short wavelength output which is the greatest dominance point of a ME tape had to be lessened as much as possible, the hard carbon film of not less than 100A of old places needs to be formed, therefore the short wavelength output was declining by not less than 2 dB.

[0007]

[Problem(s) to be Solved by the Invention]The purpose of this invention is to provide the thin film type magnetic recording medium which solves the above problems and has the outstanding corrosion resistance, still durability, and magnetic parametric performance.

[0008]

[Means for Solving the Problem]In a magnetic recording medium which the above-mentioned purpose formed a ferromagnetic thin film layer which uses Co as the main ingredients on a nonmagnetic substrate, and formed a diamond like carbon layer which uses hydrocarbon as a raw material on this ferromagnetic thin film layer, Oxygen maximum density in surface side 1 / 3 in said ferromagnetic thin film layer thickness direction is less than [ more than 10at%30at% ], and thickness of said diamond like carbon layer is attained by magnetic recording medium not less than 20A being less than 100A.

[0009]

[Function]In this invention, in order to attain said purpose, it was wholeheartedly obtained as a result of research.

The oxygen maximum density in magnetic layer surface side 1 / 3 usually accompanying [ time of vacuum evaporation ] oxygen introduction therefore, by using less than more than 10at%30at%, Decrease the spacing loss resulting from a nonmagnetic oxide layer, and 100A of diamond like carbon layers are further formed in a magnetic layer surface from 20A, Corrosion resistance and still durability are raised suppressing increase of the spacing loss resulting from a diamond like carbon layer to the minimum.

[0010]Hereafter, this invention is explained in detail.

[0011]As the magnetic recording medium of this invention is shown in drawing 1, the ferromagnetic thin film 2 is formed by vacuum evaporation on the nonmagnetic substrate 3.

The diamond like carbon layer 1 is formed on it.

A magnetic recording medium is explained in full detail below.

[0012](a) As a raw material of said nonmagnetic substrate used for nonmagnetic substrate this invention, Cellulosics, such as polyolefines, such as polyester, such as polyethylene terephthalate and polyethylene 2,6-naphthalate, and polypropylene, cellulose triacetate, and cellulose die acetate, polyamide, aromatic polyamide, polyimide, Plastics, such as a

polyphenylene sulfide, a polyether ether ketone, and polycarbonate, are used.

[0013]To said nonmagnetic substrate, the granularity or shape of a ferromagnetic metallic thin film layer is controllable by forming a vermiform protuberance and a granular projection.

[0014]Said vermiform protuberance can be formed by extending, after applying a polymeric material, for example on a nonmagnetic substrate and drying. Said granular projection. [ whether an inorganic particle with a particle diameter of 50A – about 3000A is distributed at the time of high polymer film production, and this is held inside, and ] Or it can form by distributing the particles of organic particulates or silica, and metal, and making it apply or adhere as an under-coating layer of a nonmagnetic substrate into a binder. 50A – 1000 A of height of this granular projection is 100A – 500A still more preferably. As for density, it is preferred that they are  $10^3 - 10^7$  individual / mm<sup>2</sup>. Endurance and performance traverse are improved by forming these projections.

[0015]Any, such as a tape, a sheet, a card, and a disk, may be sufficient as the gestalt of said nonmagnetic substrate, and each material is chosen according to the final gestalt as a magnetic recording medium.

[0016]The thickness of these nonmagnetic substrates is a tape and, about 3–100 micrometers in a sheet shaped, it is 4–50 micrometers preferably.

In the case of a disk and card shape, the thing of the range of 30 micrometers – 10 mm can be used.

[0017](b) A ferromagnetic thin film layer is provided on the ferromagnetic thin film layer aforementioned nonmagnetic substrate.

[0018]If the magnetic material used for this invention is an alloy system magnetic material which uses Co or Co as the main ingredients, it can use the publicly known magnetic material currently used from the former. As an example of the magnetic material used for the method of this invention, Fe-Co, Fe-Co-nickel, Co-nickel, Co-Cu, Co-Au, Co-Y, Co-La, Co-Pr, Co-Gd, Co-Sm, Co-Si, Co-Pt, Co-Cr, Fe-Co-Cr, Co-V, Co-W, Co-Mn, Co-Ti, Co-nickel-Cr, Fe-Co-nickel-Cr etc. can be mentioned.

[0019]To the ferromagnetic thin film layer in the magnetic recording medium of this invention, it is preferred that total metal atom weight contains [ Co ] 70% of the weight or more. When the content of Co is out of said range, coercive force and a residual magnetic flux density may fall, and aggravation of a magnetic parametric performance may be brought about.

[0020]Oxygen contains in a ferromagnetic thin film layer.

[0021]Usually, an oxide layer with a high oxygen density is formed near the surface of said ferromagnetic thin film layer by introducing a oxidizing gas into the low incidence air current side at the time of vacuum evaporation. The oxygen maximum density of said oxide layer

and the thickness of an oxide layer change with the introduction amounts of an oxidizing gas.

[0022] If there are too few introduction amounts of an oxidizing gas, the thickness of oxygen maximum density and an oxide layer will decrease, running durability and aggravation of corrosion-resistant and still durability are brought about, and also since the oxygen density inside a magnetic layer is also low, coercive force, an output, and S/N also become low.

[0023] On the other hand, if there are too many introduction amounts of an oxidizing gas, the thickness of the surface oxide layer of that to which coercive force becomes high will increase, and an output will decrease. As mentioned above, a good predetermined oxidizing gas introduction amount with sufficient balance of the characteristics, such as endurance, corrosion resistance, and a magnetic parametric performance, is determined.

[0024] At this time, the oxygen maximum density of a surface oxide layer will be 30 – 50at%, and the thickness of an oxide layer will be about 50–300Å.

[0025] When producing a diamond like carbon layer with a plasma CVD device on said ferromagnetic thin film layer, oxygen near the ferromagnetic thin film layer surface reacts to hydrogen or carbon by impression of negative bias voltage, and serves as H<sub>2</sub>O and CO<sub>2</sub>, and it escapes from it as gas and comes out of it. As a result, the oxygen density near [ after diamond like carbon film production ] the surface decreases compared with it before film production, spacing loss falls, and a magnetic parametric performance improves. However, if negative bias voltage is too high, abnormal discharge will be caused, and membranous deposition becomes is hard to be carried out. Within the limits of negative bias voltage of –100V––3kV is preferred.

[0026] In this invention -- the oxygen maximum density in surface side 1 / 3 of the ferromagnetic thin film layer after diamond like carbon layer film production -- 10 – 30at% -- it is 10 – 25at% preferably. As for a magnetic parametric performance, since coercive force is low, less than [ 10at% ] is [ the oxygen maximum density in surface side 1 / 3 ] insufficient, and if 30at% is exceeded, the fall of an output will be brought about by the spacing loss by a surface oxide layer.

[0027] 5000Å or less of thickness of said ferromagnetic thin film layer is within the limits of 800–3500 Å preferably.

[0028] A ferromagnetic thin film layer may comprise two or more layers, and the oxygen maximum density in surface side 1 / 3 of the ferromagnetic thin film layer top layer is 10 – 30at% in that case.

[0029] In order to form a ferromagnetic thin film layer, said ferromagnetic material is made to vapor-deposit on said nonmagnetic substrate.

[0030] As vacuum deposition, a vacuum deposition method, the ion plating method, etc. can be used. The heating can use an electron-beam–

heating method, a resistance heating method, a laser beam heating method, an induction-heating method, etc.

[0031]What is necessary is just gas which contains at least one sort chosen from the allotrope of oxygen and oxygen, and the active species of oxygen as a oxidizing gas used at the time of vacuum evaporation. As other gas which can be used together with these gases, for example Nitrogen (N<sub>2</sub>) gas, gaseous helium (helium), It is independent about inactive gas, such as xenon gas (Xe), radon gas (Rn), argon (Ar), and neon (Ne), carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), hydrogen (H<sub>2</sub>), and a steam (H<sub>2</sub>O), or two or more sorts can be mixed and used together.

[0032](c) A diamond like carbon layer is provided on the diamond like carbon layer aforementioned ferromagnetism thin film layer.

[0033]The diamond like carbon layer in this invention can use a plasma CVD device, and can produce it by decomposition of hydrocarbon gas, such as methane, ethane, propane, butane, and benzene.

[0034]The electronic structure of said diamond like carbon layer is SP<sup>2</sup> and SP<sup>3</sup>.

It is a film which consists of an amorphous state including diamond combination, and this can be judged from measurement of the binding energy by Raman analysis, TEM selected area diffraction, and ESCA.

[0035]Furthermore, Vickers hardness is highly (it measures by NEC MHA-400) excellent in abrasion resistance with Hv=2000 – 3000 (kg/mm<sup>2</sup>).

[0036]20–100 Å of thickness of said diamond like carbon layer is within the limits of 20–50 Å preferably. In less than 20Å, corrosion resistance and still durability have few effects, if it exceeds 100 Å conversely, spacing loss will increase and the fall of an output will be brought about.

[0037](d) The magnetic recording medium in other layer this inventions, An overcoat layer and a back coat layer may be provided, for example with a publicly known coating method and a deposition method after said magnetic thin film stratification and/or before formation on said nonmagnetic substrate for the purpose of the improvement of the slide nature of a magnetic recording medium, the prevention from electrification, the prevention from transfer, corrosion-resistant improvement, and wear-resistant improvement. These coating methods and a deposition method, For example, it is published by the publication-of-patent-applications specification of JP,54-123922,A, JP,54-123923,A, JP,56-71284,A, JP,56-71286,A, JP,56-71287,A, JP,56-11626,A, and JP,57-135442,A.

[0038]A back coat layer to one or more sorts of binder resin, such as VCM/PVC, VCM/PVC vinyl acetate, phenol resin, and polyurethane resin. The ferromagnetic thin film of a nonmagnetic substrate applies and forms whether two or more sorts of carbon black of the kind from which one sort, particle diameter, or chemical nature is different in conductive carbon black is distributed together, and the coating liquid distributed

independently in the opposite field in which it is provided. As an organic solvent used at the time of distribution, cyclohexanone, toluene, methyl ethyl ketone, benzene, etc. are often used. An inorganic pigment may be distributed with carbon black for surface nature or a durability improvement.

[0039]An overcoat layer as lubricant, Perfluoro polyether, piece terminal modification perfluoro polyether, both-ends denaturation perfluoro polyether, fatty acid or its metal salt, fatty acid amide, fatty acid ester, alkyl acid phosphate, acid phosphoric acid amine salt, hydrogen phosphite, Perfluoroalkyl carboxylic acid or its metal salt, perfluoroalkyl carboxylate, perfluoroalkyl sulfonic acid, Can use the ammonium salt and also Or a rust-proofer (for example, alkylphenol, hydroquinone, cresol, naphthols, and triazoles) and an extreme pressure agent. (For example, a phosphoric acid system extreme pressure agent like trio rail phosphate, a sulfur system extreme pressure agent like a methyl thioether, and a compound-die extreme pressure agent like thio phosphate) may be used together.

[0040]

[Example]Hereafter, the example of this invention is shown and this invention is explained still in detail. It cannot be overemphasized that this invention is not limited to the following examples and it can change suitably within the limits of the gist of this invention.

[0041](Example 1) It formed on the 10.0-micrometer-thick polyethylene terephthalate film using the rolling-up type vacuum deposition machine on 90 magnetic layer thetamax(es) which consist of Co-nickel=80-20 alloys, 40 thetamin, and the conditions of 2000 A of thickness. The film was produced carrying out 400SCCM introduction of the oxygen from the minimum incidence angle side.

[0042]On this sample, the plasma CVD device was used and the diamond like carbon layer was formed. Film production conditions use benzeneargon 1:1 (mole ratio) mixed gas for material gas, are 10-Pa gas pressure conditions, and produce a film considering the RF output of a plasma generation as 0.5 kW and negative bias voltage=2kV, and it was made for diamond like carbon thickness to be 20 Å. The oxygen maximum density in magnetic layer surface side 1 / 3 by the Augier depth profile was 20.2at%.

[0043]It measured about the still durability of the produced magnetic recording medium, corrosion resistance, and a magnetic parametric performance.

[0044]Still durability; after judging the produced sample to 8-mm width, it put into the cassette for 8mmVTR, and evaluated in time until it records a color bar signal first, it performs still playback after that using a commercial Hi8 VTR deck and a reproducing output declines by -2 dB from an initial value.

[0045]Corrosion resistance; after saving a tape piece for one week in 60 \*\* and 90% relative humidity, the percentage reduction of saturation magnetization was measured.

[0046]Magnetic parametric performance; the output of 7 MHz was measured using the commercial Hi8 VTR deck. However, the output of the sample which did not produce the diamond like carbon layer of the comparative example 1 here was 0 dB.

[0047]The obtained result is shown in Table 1.

[0048](Example 2) In Example 1, the magnetic recording medium was produced like Example 1 except the thickness of the diamond like carbon layer having been 30 Å. The oxygen maximum density in magnetic layer surface side 1 / 3 by the Augier depth profile was 20.8at%.

[0049](Example 3) In Example 1, the magnetic recording medium was produced like Example 1 except the thickness of the diamond like carbon layer having been 50 Å. The oxygen maximum density in magnetic layer surface side 1 / 3 by the Augier depth profile was 19.4at%.

[0050](Example 4) In Example 1, the magnetic recording medium was produced like Example 1 except the thickness of the diamond like carbon layer having been 100 Å. The oxygen maximum density in magnetic layer surface side 1 / 3 by the Augier depth profile was 19.6at%.

[0051](Example 5) In Example 1, 200SCCM introduction of the oxygen was carried out from the minimum incidence angle side, and the magnetic recording medium was produced like Example 1 except the thickness of the diamond like carbon layer having been 100 Å. The oxygen maximum density in magnetic layer surface side 1 / 3 by the Augier depth profile was 13.2at%.

[0052](Example 6) In Example 1, 600SCCM introduction of the oxygen was carried out from the minimum incidence angle side, and the magnetic recording medium was produced like Example 1 except the thickness of the diamond like carbon layer having been 20 Å. The oxygen maximum density in magnetic layer surface side 1 / 3 by the Augier depth profile was 27.3at%.

[0053](Comparative example 1) The magnetic recording medium was formed on the same conditions as Example 1 except not having produced a diamond like carbon layer in Example 1. The oxygen maximum density in magnetic layer surface side 1 / 3 by the Augier depth profile was 40.2at%.

[0054](Comparative example 2) In Example 1, the magnetic recording medium was produced like Example 1 except the thickness of the diamond like carbon layer having been 10 Å. The oxygen maximum density in magnetic layer surface side 1 / 3 by the Augier depth profile was 31.9at%.

[0055](Example 3) In Example 1, the magnetic recording medium was produced like Example 1 except the thickness of the diamond like carbon

layer having been 200 Å. The oxygen maximum density in magnetic layer surface side 1 / 3 by the Augier depth profile was 17.1at%.

[0056]

[Table 1]

ID=000003



	酸素導入量 (SCCM)	D L C 厚 (Å)	酸素最大濃度 (at%)	スチル耐久性 (min)	$\Phi_s$ 減少率 (%)	7 MHz 出力* (dB)
実施例 1	400	20	20.2	82	-11.6	+1.4
実施例 2	400	30	20.8	120 <	-8.4	+1.3
実施例 3	400	50	19.4	120 <	-6.9	+0.1
実施例 4	400	100	19.6	120 <	-6.7	-1.1
実施例 5	200	100	13.2	120 <	-7.3	-1.4
実施例 6	600	20	27.3	96	-10.1	+0.3
比較例 1	400	0	40.2	60 >	-15.3	0
比較例 2	400	10	31.9	60 >	-14.2	+0.6
比較例 3	400	200	17.1	120 <	-6.0	-2.6

\* ; ただし、比較例 1 (DLCを製膜しなかった) サンプルの出力を 0 dBとした。

[0057](Evaluation) The oxygen maximum density in surface side 1 / 3 in a ferromagnetic thin film layer thickness direction is less than [ more than 10at%30at% ] so that clearly from the above result, Examples 1-6 whose thickness of a diamond like carbon layer is not less than 20Å less than 100Å have a high output, and are low. [ of the saturation-magnetization-quantity this percentage reduction after thermostat preservation ] Still durability is also good.

[0058]

[Effect of the Invention]When producing a diamond like carbon layer on a ferromagnetic thin film layer, by impressing suitable negative bias voltage, oxygen of the ferromagnetic thin film layer surface reacts to hydrogen and carbon in early stages of film production, and in order to escape as gas and to come out, spacing loss falls. Still durability and corrosion resistance also improve by a further 20-100-Å diamond like carbon layer.

JAPANESE (JP.07-006353.A)

1. JP.07-006353.A (1995)

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT  
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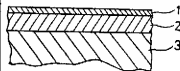
TECHNICAL FIELD

[Industrial Application] This invention relates to the magnetic recording medium which consists of a Co system ferromagnetism thin film layer, for example, magnetic tape.

[Translation done.]

Drawing selection

Representative drawing



[Translation done.]

BACK

NEXT

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PRIOR ART [Description of the Prior Art]oxide ferromagnetic powder, such as gamma-Fe<sub>2</sub>O<sub>3</sub> which contains gamma-Fe<sub>2</sub>O<sub>3</sub> and Co on a nonmagnetic substrate as a magnetic recording medium conventionally, and CrO<sub>2</sub>, -- or, The magnetic recording medium of the coating mold produced by applying and drying the magnetic paint which made powder magnetic materials, such as alloy magnetic powder which uses Fe, Co, nickel, etc. as the main ingredients, distribute in organic binders, such as a VCM/PVC system copolymer, polyester resin, and polyurethane resin, is used widely.

[0003]On the other hand, the ferromagnetic thin film formed by methods, such as vacuum deposition, sputtering, and ion plating, is examined as a magnetic recording medium for high density recording. Since these ferromagnetic thin films are not only excellent in coercive force and a remanence ratio, but do not contain an indispensable organic binder in a magnetic layer by a coating mold medium, their residual magnetic flux density is also high. Since thickness of a magnetic layer can be made very thin, there is also little thickness loss at the time of reproduction.

[0004]Thus, while it has the outstanding magnetic parametric performance, since these ferromagnetic thin films are formed from the metallic material, as compared with a coating mold medium, it is easy to be corroded, and still durability is also bad [ ferromagnetic thin films ]. [0005]In order to improve such performances, the protective layer of the amorphous carbon by weld slag or the diamond like carbon by plasma CVD is studied these days. Although it is effective in raising the performance of the above [ these hard carbon films ], by the spacing loss accompanying the thickness, especially a short wavelength output receives influence and decreases.

[0006]The short wavelength output of MP tape improves by improvement of thin-film-izing, atomization, smooth-surface-izing, etc., and it has been approaching it of a ME tape in recent years. Therefore, although the fall by the spacing loss of the short wavelength output which is the greatest dominance point of a ME tape had to be lessened as much as possible, the hard carbon film of not less than 100Å of old places needs

to be formed, therefore the short wavelength output was declining by not less than 2 dB.

1. JP 07-006353 A (1995)

JAPANESE [JP 07-006353.A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT  
OF THE INVENTION TECHNICAL PROBLEM MEANS OPERATION  
EXAMPLE DESCRIPTION OF DRAWINGS DRAWINGS

[Translation done.]

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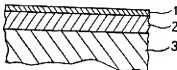
TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention]The purpose of this invention is to  
provide the thin film type magnetic recording medium which solves the above  
problems and has the outstanding corrosion resistance, still durability, and  
magnetic parametric performance.

[Translation done.]

Drawing selection

Representative drawing \*



[Translation done.]

BACK

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JAPANESE JP 07-006353 A

1. JP 07-006353 A (1995)

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT  
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EXAMPLE DESCRIPTION OF DRAWINGS DRAWINGS

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EFFECT OF THE INVENTION

[Effect of the Invention] When producing a diamond like carbon layer on a ferromagnetic thin film layer, by impressing suitable negative bias voltage, oxygen of the ferromagnetic thin film layer surface reacts to hydrogen and carbon in early stages of film production, and in order to escape as gas and to come out, spicing loss falls. Still durability and corrosion resistance also improve by a further 20-100-A diamond like carbon layer.

[Translation done.]

Drawing selection

Representative drawing \*



[Translation done.]

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JAPANESE [JP,07-006333,A]

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EXAMPLE DESCRIPTION OF DRAWINGS DRAWINGS

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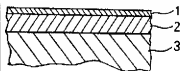
MEANS

[Means for Solving the Problem]In a magnetic recording medium which the above-mentioned purpose formed a ferromagnetic thin film layer which uses Co as the main ingredients on a nonmagnetic substrate, and formed a diamond like carbon layer which uses hydrocarbon as a raw material on this ferromagnetic thin film layer, Oxygen maximum density in surface side 1 / 3 in said ferromagnetic thin film layer thickness direction is less than [ more than 10at%30at% ], and thickness of said diamond like carbon layer is attained by magnetic recording medium not less than 20A being less than 100A.

[Translation done.]

Drawing selection

Representative drawing \*



[Translation done.]



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OPERATION [Function] In this invention, in order to attain said purpose, it was wholeheartedly obtained as a result of research.

The oxygen maximum density in magnetic layer surface side 1 / 3 usually accompanying [ time of vacuum evaporation ] oxygen introduction therefore, by using less than more than 10at%30at%, Decrease the spacing loss resulting from a nonmagnetic oxide layer, and 100A of diamond like carbon layers are further formed in a magnetic layer surface from 20A, Corrosion resistance and still durability are raised suppressing increase of the spacing loss resulting from a diamond like carbon layer to the minimum.

[0010] Hereafter, this invention is explained in detail.

[0011] As the magnetic recording medium of this invention is shown in drawing 1, the ferromagnetic thin film 2 is formed by vacuum evaporation on the nonmagnetic substrate 3.

The diamond like carbon layer 1 is formed on it.

A magnetic recording medium is explained in full detail below.

[0012] (a) As a raw material of said nonmagnetic substrate used for nonmagnetic substrate this invention, Cellulosics, such as polyolefines, such as polyester, such as polyethylene terephthalate and polyethylene 2,6-naphthalate, and polypropylene, cellulose triacetate, and cellulose diacetate, polyamide, aromatic polyamide, polyimide, Plastics, such as a polyphenylene sulfide, a polyether ether ketone, and polycarbonate, are used.

[0013] To said nonmagnetic substrate, the granularity or shape of a ferromagnetic metallic thin film layer is controllable by forming a vermiform protuberance and a granular projection.

[0014] Said vermiform protuberance can be formed by extending, after applying a polymeric material, for example on a nonmagnetic substrate and drying. Said granular projection. [ whether an inorganic particle with a particle diameter of 50A – about 3000A is distributed at the time of high polymer film production, and this is held inside, and ] Or it can form by distributing the particles of organic particulates or silica, and metal, and making it apply or adhere as an under-coating layer of a nonmagnetic substrate into a binder. 50A – 1000 A of height of this

granular projection is 100A – 500A still more preferably. As for density, it is preferred that they are 10<sup>3</sup> – 10<sup>7</sup> individual / mm<sup>2</sup>. Endurance and performance traverse are improved by forming these projections.

[0015]Any, such as a tape, a sheet, a card, and a disk, may be sufficient as the gestalt of said nonmagnetic substrate, and each material is chosen according to the final gestalt as a magnetic recording medium.

[0016]The thickness of these nonmagnetic substrates is a tape and, about about 3–100 micrometers in a sheet shaped, it is 4–50 micrometers preferably.

In the case of a disk and card shape, the thing of the range of 30 micrometers – 10 mm can be used.

[0017](b) A ferromagnetic thin film layer is provided on the ferromagnetic thin film layer aforementioned nonmagnetic substrate.

[0018]If the magnetic material used for this invention is an alloy system magnetic material which uses Co or Co as the main ingredients, it can use the publicly known magnetic material currently used from the former. As an example of the magnetic material used for the method of this invention, Fe–Co, Fe–Co–nickel, Co–nickel, Co–Cu, Co–Au, Co–Y, Co–La, Co–Pr, Co–Gd, Co–Sm, Co–Si, Co–Pt, Co–Cr, Fe–Co–Cr, Co–V, Co–W, Co–Mn, Co–Ti, Co–nickel–Cr, Fe–Co–nickel–Cr etc. can be mentioned.

[0019]To the ferromagnetic thin film layer in the magnetic recording medium of this invention, it is preferred that total metal atom weight contains [ Co ] 70% of the weight or more. When the content of Co is out of said range, coercive force and a residual magnetic flux density may fall, and aggravation of a magnetic parametric performance may be brought about.

[0020]Oxygen contains in a ferromagnetic thin film layer.

[0021]Usually, an oxide layer with a high oxygen density is formed near the surface of said ferromagnetic thin film layer by introducing a oxidizing gas into the low incidence air current side at the time of vacuum evaporation. The oxygen maximum density of said oxide layer and the thickness of an oxide layer change with the introduction amounts of a oxidizing gas.

[0022]If there are too few introduction amounts of a oxidizing gas, the thickness of oxygen maximum density and an oxide layer will decrease, running durability and aggravation of corrosion-resistant and still durability are brought about, and also since the oxygen density inside a magnetic layer is also low, coercive force, an output, and S/N also become low.

[0023]On the other hand, if there are too many introduction amounts of a oxidizing gas, the thickness of the surface oxide layer of that to which coercive force becomes high will increase, and an output will decrease. As mentioned above, a good predetermined oxidizing gas introduction amount with sufficient balance of the characteristics, such as endurance,

corrosion resistance, and a magnetic parametric performance, is determined.

[0024]At this time, the oxygen maximum density of a surface oxide layer will be 30 – 50at%, and the thickness of an oxide layer will be about 50–300Å.

[0025]When producing a diamond like carbon layer with a plasma CVD device on said ferromagnetic thin film layer, oxygen near the ferromagnetic thin film layer surface reacts to hydrogen or carbon by impression of negative bias voltage, and serves as H<sub>2</sub>O and CO<sub>2</sub>, and it escapes from it as gas and comes out of it. As a result, the oxygen density near [ after diamond like carbon film production ] the surface decreases compared with it before film production, spacing loss falls, and a magnetic parametric performance improves. However, if negative bias voltage is too high, abnormal discharge will be caused, and membranous deposition becomes is hard to be carried out. Within the limits of negative bias voltage of -100V--3kV is preferred.

[0026]In this invention -- the oxygen maximum density in surface side 1 / 3 of the ferromagnetic thin film layer after diamond like carbon layer film production -- 10 – 30at% -- it is 10 – 25at% preferably. As for a magnetic parametric performance, since coercive force is low, less than [ 10at% ] is [ the oxygen maximum density in surface side 1 / 3 ] insufficient, and if 30at% is exceeded, the fall of an output will be brought about by the spacing loss by a surface oxide layer.

[0027]5000Å or less of thickness of said ferromagnetic thin film layer is within the limits of 800–3500 Å preferably.

[0028]A ferromagnetic thin film layer may comprise two or more layers, and the oxygen maximum density in surface side 1 / 3 of the ferromagnetic thin film layer top layer is 10 – 30at% in that case.

[0029]In order to form a ferromagnetic thin film layer, said ferromagnetic material is made to vapor-deposit on said nonmagnetic substrate.

[0030]As vacuum deposition, a vacuum deposition method, the ion plating method, etc. can be used. The heating can use an electron-beam-heating method, a resistance heating method, a laser beam heating method, an induction-heating method, etc.

[0031]What is necessary is just gas which contains at least one sort chosen from the allotrope of oxygen and oxygen, and the active species of oxygen as a oxidizing gas used at the time of vacuum evaporation. As other gas which can be used together with these gases, for example Nitrogen (N<sub>2</sub>) gas, gaseous helium (helium), It is independent about inactive gas, such as xenon gas (Xe), radon gas (Rn), argon (Ar), and neon (Ne), carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), hydrogen (H<sub>2</sub>), and a steam (H<sub>2</sub>O), or two or more sorts can be mixed and used together.

[0032](c) A diamond like carbon layer is provided on the diamond like carbon layer aforementioned ferromagnetism thin film layer.

[0033]The diamond like carbon layer in this invention can use a plasma CVD device, and can produce it by decomposition of hydrocarbon gas, such as methane, ethane, propane, butane, and benzene.

[0034]The electronic structure of said diamond like carbon layer is SP<sup>2</sup> and SP<sup>3</sup>.

It is a film which consists of an amorphous state including diamond combination, and this can be judged from measurement of the binding energy by Raman analysis, TEM selected area diffraction, and ESCA.

[0035]Furthermore, Vickers hardness is highly (it measures by NEC MHA-400) excellent in abrasion resistance with Hv=2000 - 3000 (kg/mm<sup>2</sup>).

[0036]20-100 Å of thickness of said diamond like carbon layer is within the limits of 20-50 Å preferably. In less than 20Å, corrosion resistance and still durability have few effects, if it exceeds 100 Å conversely, spacing loss will increase and the fall of an output will be brought about.

[0037](d) The magnetic recording medium in other layer this inventions, An overcoat layer and a back coat layer may be provided, for example with a publicly known coating method and a deposition method after said magnetic thin film stratification and/or before formation on said nonmagnetic substrate for the purpose of the improvement of the slide nature of a magnetic recording medium, the prevention from electrification, the prevention from transfer, corrosion-resistant improvement, and wear-resistant improvement. These coating methods and a deposition method, For example, it is published by the publication-of-patent-applications specification of JP,54-123922,A, JP,54-123923,A, JP,56-71284,A, JP,56-71286,A, JP,56-71287,A, JP,56-11626,A, and JP,57-135442,A.

[0038]A back coat layer to one or more sorts of binder resin, such as VCM/PVC, VCM/PVC vinyl acetate, phenol resin, and polyurethane resin. The ferromagnetic thin film of a nonmagnetic substrate applies and forms whether two or more sorts of carbon black of the kind from which one sort, particle diameter, or chemical nature is different in conductive carbon black is distributed together, and the coating liquid distributed independently in the opposite field in which it is provided. As an organic solvent used at the time of distribution, cyclohexanone, toluene, methyl ethyl ketone, benzene, etc. are often used. An inorganic pigment may be distributed with carbon black for surface nature or a durability improvement.

[0039]An overcoat layer as lubricant, Perfluoro polyether, piece terminal modification perfluoro polyether, both-ends denaturation perfluoro polyether, fatty acid or its metal salt, fatty acid amide, fatty acid ester, alkyl acid phosphate, acid phosphoric acid amine salt, hydrogen phosphite, Perfluoroalkyl carboxylic acid or its metal salt, perfluoroalkyl carboxylate, perfluoroalkyl sulfonic acid, Can use the ammonium salt and also Or a rust-proofer (for example, alkylphenol, hydroquinone, cresol,

naphthols, and triazoles) and an extreme pressure agent. (For example, a phosphoric acid system extreme pressure agent like trio rail phosphate, a sulfur system extreme pressure agent like a methyl thioether, and a compound-die extreme pressure agent like thio phosphate) may be used together.

[Translation done.]

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EXAMPLE [Example] Hereafter, the example of this invention is shown and this invention is explained still in detail. It cannot be overemphasized that this invention is not limited to the following examples and it can change suitably within the limits of the gist of this invention.

[0041] (Example 1) It formed on the 10.0-micrometer-thick polyethylene terephthalate film using the rolling-up type vacuum deposition machine on 90 magnetic layer thetamax(es) which consist of Co-nickel=80-20 alloys, 40 thetamin, and the conditions of 2000 A of thickness. The film was produced carrying out 400SCCM introduction of the oxygen from the minimum incidence angle side.

[0042] On this sample, the plasma CVD device was used and the diamond like carbon layer was formed. Film production conditions use benzeneargon 1:1 (mole ratio) mixed gas for material gas, are 10-Pa gas pressure conditions, and produce a film considering the RF output of a plasma generation as 0.5 kW and negative bias voltage-2kV, and it was made for diamond like carbon thickness to be 20 A. The oxygen maximum density in magnetic layer surface side 1 / 3 by the Augier depth profile was 20.2at%.

[0043] It measured about the still durability of the produced magnetic recording medium, corrosion resistance, and a magnetic parametric performance.

[0044] Still durability; after judging the produced sample to 8-mm width, it put into the cassette for 8mmVTR, and evaluated in time until it records a color bar signal first, it performs still playback after that using a commercial Hi8 VTR deck and a reproducing output declines by -2 dB from an initial value.

[0045] Corrosion resistance; after saving a tape piece for one week in 60 \*\* and 90% relative humidity, the percentage reduction of saturation magnetization was measured.

[0046] Magnetic parametric performance; the output of 7 MHz was measured using the commercial Hi8 VTR deck. However, the output of the sample which did not produce the diamond like carbon layer of the comparative example 1 here was 0 dB.

[0047] The obtained result is shown in Table 1.

[0048](Example 2) In Example 1, the magnetic recording medium was produced like Example 1 except the thickness of the diamond like carbon layer having been 30 Å. The oxygen maximum density in magnetic layer surface side 1 / 3 by the Augier depth profile was 20.8at%.

[0049](Example 3) In Example 1, the magnetic recording medium was produced like Example 1 except the thickness of the diamond like carbon layer having been 50 Å. The oxygen maximum density in magnetic layer surface side 1 / 3 by the Augier depth profile was 19.4at%.

[0050](Example 4) In Example 1, the magnetic recording medium was produced like Example 1 except the thickness of the diamond like carbon layer having been 100 Å. The oxygen maximum density in magnetic layer surface side 1 / 3 by the Augier depth profile was 19.6at%.

[0051](Example 5) In Example 1, 200SCCM introduction of the oxygen was carried out from the minimum incidence angle side, and the magnetic recording medium was produced like Example 1 except the thickness of the diamond like carbon layer having been 100 Å. The oxygen maximum density in magnetic layer surface side 1 / 3 by the Augier depth profile was 13.2at%.

[0052](Example 6) In Example 1, 600SCCM introduction of the oxygen was carried out from the minimum incidence angle side, and the magnetic recording medium was produced like Example 1 except the thickness of the diamond like carbon layer having been 20 Å. The oxygen maximum density in magnetic layer surface side 1 / 3 by the Augier depth profile was 27.3at%.

[0053](Comparative example 1) The magnetic recording medium was formed on the same conditions as Example 1 except not having produced a diamond like carbon layer in Example 1. The oxygen maximum density in magnetic layer surface side 1 / 3 by the Augier depth profile was 40.2at%.

[0054](Comparative example 2) In Example 1, the magnetic recording medium was produced like Example 1 except the thickness of the diamond like carbon layer having been 10 Å. The oxygen maximum density in magnetic layer surface side 1 / 3 by the Augier depth profile was 31.9at%.

[0055](Example 3) In Example 1, the magnetic recording medium was produced like Example 1 except the thickness of the diamond like carbon layer having been 200 Å. The oxygen maximum density in magnetic layer surface side 1 / 3 by the Augier depth profile was 17.1at%.

[0056]

[Table 1]

ID=000003

	酸素導入量 (SCCM)	D L C 厚 (Å)	酸素最大濃度 (at%)	スチル耐久性 (min)	$\Phi_s$ 減少率 (%)	7MHz 出力* (dB)
例1	400	20	20.2	82	-11.6	+1.4
例2	400	30	20.8	120 <	-8.4	+1.3
例3	400	50	19.4	120 <	-6.9	+0.1
例4	400	100	19.6	120 <	-6.7	-1.1
例5	200	100	13.2	120 <	-7.3	-1.4
例6	600	20	27.3	96	-10.1	+0.3
例1	400	0	40.2	60 >	-15.3	0
例2	400	10	31.9	60 >	-14.2	+0.6
例3	400	200	17.1	120 <	-6.0	-2.6

\* ; ただし、比較例1 (DLCを製膜しなかった) サンプルの出力を0 dBとした。



[0057](Evaluation) The oxygen maximum density in surface side 1 / 3 in a ferromagnetic thin film layer thickness direction is less than [ more than 10at%30at% ] so that clearly from the above result, Examples 1-6 whose thickness of a diamond like carbon layer is not less than 20Å less than 100Å have a high output, and are low. [ of the saturation-magnetization-quantity this percentage reduction after thermostat preservation ] Still durability is also good.

[Translation done.]

DOCUMENT 1/2  
DOCUMENT NUMBER  
#: unavailable

**JAPANESE** [JP,07-006353,A]

Drawing  
selection

1. JP,07-006353,A(1995)
2. JP,08-102052,A(1996)

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL  
PROBLEM MEANS OPERATION EXAMPLE DESCRIPTION OF DRAWINGS DRAWINGS

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is an important section expanded sectional view of the magnetic recording medium of this invention.

[Description of Notations]

- 1 Diamond like carbon layer
- 2 Magnetic layer
- 3 Nonmagnetic substrate (substrate)

[Translation done.]

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DOCUMENT 1/2  
DOCUMENT NUMBER  
@: unavailable

1. JP.07-006353.A(1995)
2. JP.08-102052.A(1996)

**JAPANESE** [JP.07-006353.A]

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DRAWINGS

[Drawing 1]



[Translation done.]

Drawing  
selection

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